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(54) **Polymer-containing granulates**

Polymer enthaltende Granulate

Granulés contenant des polymères

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(56) References cited:  
**EP-A- 0 200 163**                      **EP-A- 0 256 443**  
**EP-A- 0 289 768**                      **WO-A-90/05175**  
**FR-A- 2 401 987**                      **US-A- 4 414 130**

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## Description

[0001] This invention is concerned with polymer-containing granules useful as a component for detergent formulations. In the following, "detergent formulations" is intended to encompass cleaning agents for both fabrics and hard surfaces.

[0002] For environmental reasons it has become desirable to reduce or eliminate the phosphate content of detergent formulations. Consequently a replacement component which would provide similar properties, such as inhibition of salt and soil redeposition on washed fabric, and hard surfaces and improved whiteness, must be added. Polymeric additives, especially polycarboxylated polymers, are suitable for this purpose.

[0003] Polymers are generally added to detergent formulations either in the form of a dry powder, formed by spray-drying a solution, dispersion, slurry or emulsion of polymer in a liquid ('wet polymer'), or directly as wet polymer to a detergent formulation in slurry form before drying. In both cases, the final product has a number of undesirable features.

[0004] The dry powder formed by spray-drying wet polymer alone is a material which is hygroscopic and therefore tends to become 'sticky' upon storage or in the final formulation itself. Such dry polymer also has a low bulk density, typically 300-500 g/l, which means that in a typical detergent formulation having density in the region of 700 g/l the polymer has a tendency to separate out; it also reduces the bulk density of the formulation. Furthermore, the dry polymer powder usually has a high proportion of fine material, leading to undesirable dusting problems in the final formulation, and further contributing to the problem of separation.

[0005] One method of adding wet polymer is to add it to other components of the final formulation before drying, and then to spray-dry the polymer and other components together. An example of a granulate composition made by such a method is disclosed in DE-A-3316513, in which a granule for use as a phosphate substitute, containing 30-75% zeolite together with at least 5% polycarboxylate, is made by spray-drying a slurry of the components. Such a spray-drying process invariably yields a granulated product of undesirably low density, and indeed the highest density achieved by this composition is 610 g/l; also, additional water - that introduced with the polymer - has to be removed.

[0006] An alternative method for adding wet polymer is to add it directly to the final formulation as it is mixed and dried in a rotating drum mixer. However wet polymer contains liquid (usually water) and polymer in a ratio of about 1:1, so that adding more than just a few percent of polymer requires the addition of a significant amount of liquid also: solubilization by the liquid of other components in the formulation tends to result in the formulation of a paste in the dryer. This problem cannot be avoided by reducing the liquid content of the polymer prior to addition, because the viscosity of the wet poly-

mer becomes too high for satisfactory flowability and even distribution of the polymer amongst the other components.

[0007] The above method of adding wet polymer may be used when polymers are to be employed as agglomerating agents for salts; in such a case they are added at concentrations of only about 0.5%, so that the difficulties with excess liquid become insignificant.

[0008] The above problems also cannot be avoided by adding the polymer to solutions of other salts to be used in the final formulation such as sulphates and carbonates, and then drying by evaporation, because the polymers used are effective crystallization inhibitors for those salts.

[0009] In summary therefore, forms of dry polymer hitherto produced have proved unsatisfactory for detergent formulations in that (i) the polymer dried alone has particle size, hygroscopicity and density disadvantages and (ii) the polymer dried in the presence of the remainder of the formulation induces paste formation if dried in spray-mixing equipment or reduces to too low a density if dried in a spray tower. There was no indication, indeed the experience in (ii) contraindicated, that the polymer could be successfully combined with some of the other components for the detergent formulation into a granular form, having desirable particle size and bulk density, for addition to the detergent formulation.

[0010] Granules having densities of from 300 to 800 g/l are known from FR-A-2401907. They generally comprise zeolite and a binder such as starch, cellulose or certain nonionic surfactants. However, no granules containing the polycarboxylated polymers typically used as phosphate replacements are disclosed.

[0011] A high density polymer-containing granulate is known, from EP-A-368137; it contains 60-80% zeolite, 2-15% polycarboxylate, and 14-25% by weight of water, and has a density of 750-1000 g/l. However, the presence of such a large proportion of water insoluble zeolite brings disadvantages. Water-insoluble salts have a tendency to deposit on fabrics, a problem which the addition of polymers is at least partly intended to counteract; in a granule containing such a high ratio of water-insoluble salt to polymer, any effect as a suspending agent which the polymer might have been intended to have would be virtually nullified by the large amount of zeolite introduced with the polymer.

[0012] A granular detergent additive is known from US-A-4698174 which comprises 20-80% polymer, 20-80% nitrilotriacetic acid (NTA) and optionally up to 20% of another additive such as sodium sulphate. Densities of up to 690 g/l are disclosed, and the product is also said to have low hygroscopicity. However, the usefulness of this additive is limited by the necessity for it to comprise a significant proportion of NTA to obtain satisfactory performance; large proportions of NTA may be considered undesirable on environmental grounds. Furthermore the densities disclosed are still generally less than the average density of a typical detergent.

**[0013]** In a first aspect the present invention provides a composition, useful as a component of a detergent formulation, in the form of granules each comprising at least 10% by weight of polycarboxylated polymer useful in such formulations and at least 20% by weight of at least one water-soluble inorganic component also useful in such formulations, the bulk density of said composition being at least 700 g/l. Preferred inorganic components are salts, such as sulphates, carbonates and silicates. Perborates (both mono- and tetrahydrate), percarbonates and persulphates may also be useful. In formulations where phosphates are still present, they may also be used as carriers. For all the above salts, the sodium form is preferred.

**[0014]** The present invention is also applicable to the case where the inorganic component is zeolite or clay, which are both water-insoluble. In such a case, a greater proportion of polymer is necessary in order to counteract the tendency of the water-insoluble component to deposit on fabrics, as indicated above. Accordingly in a second aspect the present invention provides a composition, useful as a component in detergent formulations, in the form of granules each comprising at least 20% by weight of polycarboxylated polymer useful in such formulations and at least 20% by weight of zeolite, the bulk density of said composition being at least 700 g/l, wherein the polycarboxylated polymer is a homopolymer or copolymer of one or more of acrylic acid, methacrylic acid, maleic acid, itaconic acid, and (C<sub>1</sub>-C<sub>4</sub>)alkyl (meth)acrylates or amides, acrylamide, alpha-chloroacrylic acid, alkylvinylether or vinylesters.

**[0015]** It will be appreciated that in both cases the granules may contain minor amounts of other components which are suitable for use in detergent compositions.

**[0016]** The density of the granulate may be as high as 1400 g/l, although a density in the range from 700 to 1200 g/l is preferred, particularly over 900 g/l. The density depends on the type of organic component ("carrier"), on polymer type, and on manufacturing process conditions and equipment (discussed hereinafter), and also on the relative proportions of polymer(s) and carrier(s). Thus granules containing up to 80% polymer by weight may be prepared. In this case, the density of such granules will be at the bottom end of the desired range. Typically 10% to 50% by weight polymer is present in the granule (but at least 20%, preferably at least 25% where zeolite is present), and more typically from 20% to 40%. The most preferred amount of polymer is 30%.

**[0017]** Suitable polycarboxylated polymers include homopolymers of dicarboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, citraconic acid and the anhydrides of cis dicarboxylic acids, such as maleic anhydride; monocarboxylic acids such as acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid and acryloxypropionic acid; copolymers of the aforementioned carboxylic acids; and copolymers of one or more of the aforementioned carboxylic acids and

unsaturated non-carboxylic acids such as alkyl esters of acrylic or methacrylic acids such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and isobutyl methacrylate; hydroxyalkyl esters of acrylic or methacrylic acids such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate (including polyethoxylated esters); acrylamide, methacrylamide, N-tertiary butyl acrylamide, N-methyl acrylamide, N,N-dimethyl acrylamide; acrylonitrile, methacrylonitrile, allyl alcohol, allyl sulfonic acid, allyl phosphonic acid, vinylphosphonic acid, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, phosphoethyl methacrylate, N-vinyl pyrrolidone, N-vinylformamide, N-vinylimidazole, ethylene glycol diacrylate, trimethylolpropane triacrylate, diallyl phthalate, vinyl acetate, styrene, vinyl sulfonic acid and its salts, 2-acrylamido-2-methyl propane sulfonic acid (AMPS) and its salts, monomers of 1-olefins, such as diisobutylene and 1-octene and the polymer "POC" (the reaction product of acrylic acid and peroxodisulphate).

**[0018]** Polymers can be in acid or neutralized or partially neutralized form with Na, K, NH<sub>4</sub> or other counterions. Molecular weights of the polymers may be from 500 to 5,000,000. Generally the higher molecular weight, the greater the degree of agglomeration obtained during manufacture of the granules and hence the larger the granules. Thus the choice of molecular weight will be at least partly dependent on the granulometry of the product required.

**[0019]** Examples of polymers employed in the present invention are an acrylic acid homopolymer having a weight-average molecular weight of 4500 and an acrylic/maleic copolymer having a weight-average molecular weight of about 70,000.

**[0020]** The granules of the present invention can have a wide range of size distributions, from 1 micron to 2mm or more in diameter. Granulates with up to 80-% particles on 14 U.S. mesh (mesh size 1.18 mm) or with up to 80% particles through 100 U.S. mesh (mesh size 0.15 mm) can be produced. It is preferred that less than 50% by weight pass through 100 U.S. mesh. In a preferred option, the size of the granules formed is such that it approximates to the average size of particles in a standard detergent composition (0.2-0.4mm typically).

**[0021]** The granular composition of the invention provides polymer suitable for use in detergent formulations in a form which has considerable advantages over the prior art. The dry granule may be added direct to the final formulation, thereby circumventing all the disadvantages associated with wet polymer. The composition can be adjusted to have a granulometry and density very similar to that of the other components in the final formulation, thereby avoiding the problems of separation and dusting associated with spray-dried polymer. Furthermore, the granular composition of the present invention does not suffer from the problems of hygroscopicity which affects spray-dried polymer. The larger particu-

late size means that there is less surface area per unit weight to absorb moisture, and also the proportion of hygroscopic polymer in each granule is obviously less than in 'dry polymer' powder. For the purposes of the present invention, a granulate which absorbs less than 20% of its own weight in water when exposed to moisture is preferred, particularly less than 10%. The method employed to determine this percentage of water absorption is as follows:

**[0022]** A previously weighed container is placed in an air-conditioned room at a temperature of 20°C and humidity of 50%, filled with a thin layer (5-20mm) of polymer and immediately reweighed, at which point the test starts. The container and polymer are then reweighed at ten minute intervals during the first hour, 30 minute intervals during the second hour, hourly during the next five hours and then every 24 hours. The percentage increase in weight gives the amount of water absorbed, and the figure quoted is that attained when a steady state has been reached.

**[0023]** Thus the present invention has successfully solved the problem of obtaining polymer in a form which is acceptable for direct addition to detergent formulations, without the attendant problems either of the liquid carrier associated with the polymer, or of the consequences of having removed that liquid carrier first. Furthermore, the present invention provides a much more flexible solution to the previous problems than known compositions such as those described hereinabove, in that there is a wide variety of inorganic components which can be incorporated with the polymer, with no individual compound being an essential prerequisite. Additionally, the density of the composition of the invention can be significantly higher than that possible with known compositions.

**[0024]** The present invention also provides, in further aspect, a detergent formulation containing polymer in the form of a composition as defined above; and in a still further aspect it comprises the use of a composition as defined above as a component in a detergent formulation. The proportion of the granulate composition of this invention required in a typical detergent formulation will generally be such as to give an active polymer content in the formulation of from 0.1 to 20% by weight, more usually between 1 and 5%.

**[0025]** Typical detergents for which the granular composition of the present invention may be suitable are usually based on surfactants and, optionally, on either precipitant or sequestrant builders. Suitable surfactants are, for example, anionic surfactants, such as (C<sub>8</sub> to C<sub>12</sub>) alkylbenzenesulfonates, (C<sub>12</sub> to C<sub>16</sub>) alkane sulfonates, (C<sub>12</sub> to C<sub>16</sub>) alkylsulfates, (C<sub>12</sub> to C<sub>16</sub>) alkylsulfosuccinates and (C<sub>12</sub> to C<sub>16</sub>) sulfated ethoxylated alkanols. Nonionic surfactants may be (C<sub>6</sub> to C<sub>12</sub>) alkylphenol ethoxylates, (C<sub>12</sub> to C<sub>20</sub>) alkanol alkoxylates, and block copolymers of ethylene oxide and propylene oxide. Optionally, the end groups of polyalkylene oxides can be blocked. This means the free OH groups of the

polyalkylene oxides can be etherified, esterified, acetalised and/or aminated. Another modification consists of reacting the free -OH groups of the polyalkylene oxides with isocyanates.

**[0026]** Nonionic surfactants may also include (C<sub>4</sub> to C<sub>18</sub>) alkyl glucosides as well as the alkoxyated products obtainable therefrom by alkoxylation, particularly those obtainable by reaction of alkyl glucosides with ethylene oxide. Surfactants useful in detergents can also have an amphoteric character and they can be soaps. In general, the surfactants constitute from 2 to 50 wt % of a detergent.

**[0027]** Sequestrant builders contained in detergents have generally been phosphates, orthophosphates, pyrophosphates or especially sodium tripolyphosphate. However, because of the severe environmental pollution caused by the use of phosphates, the phosphate content of detergents and cleaning agents is increasingly being reduced so that detergents currently contain up to 25% of phosphates or preferably are phosphate-free. As discussed previously, the composition of the present invention is primarily of value as a means for introducing into the detergent a partial or complete replacement for phosphates, comprising polymers as previously listed. Other builders include zeolites, sodium carbonate, nitrilotriacetic acid, citric acid, tartaric acid, the salts of the aforesaid acids and the monomeric, oligomeric or polymeric phosphonates. Varying amounts of the individual substances are used in the preparation of detergent formulations. For example, sodium carbonate may be used in an amount of up to 80%, phosphates up to 80%, zeolites up to 40%, nitrilotriacetic acid and phosphonates up to 10% and polycarboxylic acids in an amount of up to 30% by weight based on the total detergent formulation.

**[0028]** Typical detergent formulations optionally also contain corrosion inhibitors, such as silicates as additional additives. Suitable silicates are, for example, sodium silicate, sodium disilicate and sodium metasilicate. The corrosion inhibitors can constitute up to 50 wt % of the detergent formulation. Other common additives to detergent and cleaning agent formulations are bleaching agents used in an amount of up to 30 wt %. Suitable bleaching agents are for example, perborates, percarbonates, or chlorine-generating substances, such as chloroisocyanurates. Another group of additives that can be used in detergents are greying inhibitors. Known substances of this type are carboxymethylcellulose, methylcellulose, hydroxypropylmethylcellulose and graft copolymers of vinyl acetate and polyalkylene oxides having a molecular weight of 1000 or 15,000. Greying inhibitors are used in the detergent formulations in an amount of up to 5%. Other common detergent additives that can optionally be used are optical brighteners, enzymes and perfume. Powdered detergent formulations can also contain up to 50 wt % of a diluent, such as sodium sulfate. The detergent formulations can be anhydrous or they can obtain small amounts, for exam-

ple up to 10 wt %, of water.

**[0029]** The composition of the present invention may be made by a process according to a further aspect of the invention, which comprises mixing polycarboxylated polymer useful in detergent compositions with a liquid suitable for carrying or solubilizing said polymer and at least one solid inorganic component, the ratio of polymer to inorganic component being from 1:9 to 5:1, and subjecting the mixture to conditions of agitation and heat such that granules are formed. Generally the polymer and liquid are introduced together - as a slurry, solution, emulsion, suspension or dispersion of polymer in liquid. Preferably the granules formed are as defined herein above.

**[0030]** The particular conditions of heat and agitation which are required in order to produce the desired granules are complex, and dependent on a large number of interrelated variables. It is highly important that the polymer, liquid and inorganic component are subjected to a degree of turbulence such that rapid and intimate mixing, plus uniform heating is achieved; additionally a rapid and effective rate of heat transfer is required in order to evaporate the liquid very soon after the mixture is formed, especially when the inorganic component is soluble in the liquid.

**[0031]** In a preferred embodiment of the process which achieves the above requirements, the components are mixed in a horizontal cylindrical chamber having an axial shaft which carries a series of radial blades extending almost to the wall of the chamber, which forces the mixture into a highly turbulent thin layer around the wall of the chamber. A pressure differential moves the mixture along the chamber, where it is additionally subjected to heating by one or both of hot air blown through the chamber and heating of the chamber wall in contact with the mixture layer. The mixture may be subjected to heating as soon as it enters the chamber; alternatively, heat may be applied after the mixture has passed a little way along the chamber, so that initial mixing occurs before the commencement of evaporation. This alternative procedure may also be embodied by employing two chambers, in series, the first of which subjects the mixture solely to high agitation and the second of which subjects it both to agitation and to heating. This method allows greater control of the degree of turbulence at each stage, although, for reasons outlined above, care may be needed in determining the residence time in the initial mixing chamber to ensure that evaporation does not commence too late.

**[0032]** Although the chamber(s) is preferably horizontal, this is not essential and it may be inclined or even vertical.

**[0033]** The unique combination of turbulence and rate of heat transfer provided by the process of this invention results in a product which was not previously achievable. The granules produced are generally an agglomeration of many particles, each particle comprising a core of inorganic component ('carrier') coated with a layer of

polymer, although under certain conditions a homogeneous mixture may be formed. The process of the invention is particularly advantageous in the case where the inorganic component is soluble in the liquid (usually water) carrying the polymer. An example is where the inorganic component is a sulphate, which is soluble in water. In such a case, the evaporation of the liquid in this process is so rapid that solubilization of the inorganic carrier occurs only to an extent which is insufficient to deleteriously affect the density or particle size of the final granulate product. This would be impossible with conventional techniques.

**[0034]** As mentioned above, the parameters influencing the nature of the final product are many and complex. The relative proportions of polymer and carrier are significant; increasing the proportion of polymer reduces the density of the final granules, and also results in larger granules by causing more agglomeration. The nature of the components is also significant. As discussed previously, the molecular weight of the polymer can influence the granulometry of the final product. It can be advantageous for the inorganic component to be an anhydrous salt, since this will absorb water carrying the polymer during mixing, thereby leaving less to be evaporated and speeding the process. The two main process conditions which need to be influenced are the rate of heat transfer to the components as they are being mixed, and the degree of turbulence of that mixing. As a generalisation, increasing either the rate of heat transfer or the turbulence reduces the degree of agglomeration, and hence the size of the particles.

**[0035]** The rate of heat transfer may be enhanced by increasing either the temperature or the flowrate of the hot air which is passed through the chamber, or by increasing the temperature of the heating jacket around the wall of the chamber. As discussed previously, the positions of the hot air inlet and the heating jacket may also be adjusted to influence the timing and rate of heat transfer. The initial temperature of the liquid carrying the polymer may also be varied; increasing this not only improves the evaporation capacity of the apparatus, but also the homogeneity of the final granule by reducing the initial viscosity of the liquid/polymer system. The rate of heat transfer is also increased by greater turbulence.

**[0036]** The turbulence of the mixture in the chamber may be increased by increasing the speed of rotation of the shaft and blades. It is also influenced by the nature of the blades - their number, shape, orientation, etc; it will be appreciated that the precise effect of the blades is a matter for assessment in each case.

**[0037]** Another factor of significance is the residence time of the mixture in the chamber - i.e. the length of time of its exposure to heating and/or turbulent mixing, which has to be adjusted to provide the optimum balance. The mixture is drawn through the chamber largely by a pressure differential, variation of which will of course alter the residence time. The length of the chamber - or separation into a mixing and a mixing/heating

chamber - is another influencing factor.

[0038] Preferred embodiments of both the process and the composition of the invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic representation of an agglomerating apparatus suitable for performing a preferred process of the invention;

Figures 2 to 4 are graphs showing the granulometry of compositions of the invention.

[0039] Referring to Figure 1, preferred apparatus for the agglomeration process of the invention comprises a horizontal cylindrical chamber 2 having at one end inlets 4,6 for the liquid/polymer system and dry inorganic carrier respectively, and at its other end an outlet 8 for the granulated product. An air compressor 22 pushes the air (and hence the material) along the chamber, and a fan 10 contributes to a pressure drop which also helps to draw the material through.

[0040] Heating is accomplished partly by hot air injected into the chamber through inlet 12, and partly by a coaxial heating jacket 14 around the chamber. Hot air inlet 12 and jacket 14 are spaced along the chamber from the raw material inlets 4,6 so that material in the initial portion of the chamber is not subjected to heating, but only to mixing. As discussed previously, in an alternative embodiment this initial mixing without heating phase (which is not always essential) may be performed in a separate chamber.

[0041] Turbulent mixing is accomplished by means of a rapidly rotating axial shaft 16 which carries a series of blades 18 each extending radially towards the wall of the chamber. In this embodiment each blade is substantially rectangular, and its outer edge is spaced from the internal wall of the chamber 2 by a few millimetres (this spacing being adjustable). Shaft 16 is driven by a motor 20. In certain embodiments movement of the material along the chamber may be accomplished solely by the rotating blades, without the need for a pressure differential.

[0042] The operation of the apparatus of Figure 1 is as follows, described with reference to a preferred composition comprising a polymer/water system.

[0043] Dry carrier and a solution of polymer in water enter the chamber 2 through respective inlets 4,6. The polymer solution may already be at elevated temperature in order to reduce its viscosity and improve mixing. Inside the chamber the shaft 16 and its blades 18 are rotated at a high rate, typically from 500 to 3000 rpm. The rate employed depends of course on factors such as the diameter of the drum, since the important parameter is the tangential velocity imparted to the mixture at the surface of the chamber wall (in this particular embodiment the tangential velocity is generally from 10 to 30 ms<sup>-1</sup>).

[0044] The mixture of polymer, water and carrier is

drawn through the chamber by the combined action of compressor 22 and fan 10, whilst the centrifugal force created by the rapidly rotating blades 18 forces the mixture into a highly dynamic suspension in the form of a thin layer around the internal surface of the chamber wall. The precise thickness of the layer depends on a number of factors, particularly the degree of centrifugal force exerted on it, but it is approximately 1-2 mm. The blades are preferably arranged to extend close enough to the chamber wall that their outer edges contact and disrupt the layer of agglomerating mixture, thereby generating further turbulence and inhibiting the development of excessively large granules.

[0045] The residence time of the mixture in the initial unheated portion of the chamber is very short - of the order of a few seconds. It is especially important if the carrier is soluble in water that the carrier does not begin to dissolve before evaporation of the water begins. Of course, if necessary the apparatus may be arranged so that the mixture is subjected to heating as soon as it enters the mixing chamber.

[0046] After this initial mixing phase, the mixture is subjected to heating by hot air injected through inlet 12 and saturated steam passing around jacket 14. Together these provide a very efficient combination of both convective and conductive heat transfer, resulting in rapid evaporation of the water from the mixture. The continuous rotation of the mixture layer and individual particles within it provides ideal conditions of turbulence and particle separation, permitting uniform heating and excellent agglomeration.

[0047] The mixture reaches outlet 8 after a time period of from around 10 seconds to a few minutes, by which time it has agglomerated into dense, dry granules of polymer and carrier, with the water being removed as vapour.

[0048] Specific examples of granulated compositions of the present invention produced by the above exemplified process are as follows:

#### Example 1:

[0049] A granulate containing 30% dry polymer is obtained as follows: 100 kg/h of sodium sulphate and 95 kg/h of a 45% water solution of an acrylic acid homopolymer having a weight average molecular weight of 4500 are fed continuously into the mixer chamber.

[0050] The shaft speed rotation is 900 rpm, the hot air is fed (co-currently with the granule flow) into the mixing chamber at 225°C and 280 m<sup>3</sup>/h. Saturated steam at 160°C is fed into the jacket.

[0051] Finished product (granulates) is discharged continuously starting about one minute after the operation start-up, at 143 kg/h, 0.5% residual moisture and 100°C. The density of the product is 1000 g/lit and the granulometry spectrum, compared with leading fabric wash detergents, is shown in Figure 2.

**Example 2:**

[0052] A product containing 10% dry polymer is obtained by employing the same process conditions as Example 1, but with 100 kg/h of sodium sulphate and 28 kg/h of an acrylic/maleic copolymer having a weight average molecular weight of 70,000.

[0053] Density of the granulates is 1200 g/l, and the granulometry distribution is shown in Figure 3.

**Example 3:**

[0054] A product containing 30% dry polymer is obtained as follows: 120 kg/h of sodium carbonate and 115 kg/h of the polymer of Example 1 are fed continuously into the mixing chamber. The shaft speed rotation is 1800 rpm, the hot air is fed co-currently at 200°C. Saturated steam at 180°C is fed into the jacket. Finished product is obtained at 1% residual moisture at 70°C. The density of the product is 860 g/l and the granulometry spectrum is shown in Figure 4.

**Claims**

1. Granules, useful as a component in detergent formulations, each comprising at least 10% by weight of a polycarboxylated polymer useful in such formulations and at least 20% by weight of at least one water-soluble inorganic component also useful in such formulations, the bulk density of said granules being at least 700 g/l.
2. Granules according to Claim 1, wherein said inorganic component is one or more of sulphate, carbonate, phosphate, silicate, percarbonate or perborate, preferably sulphate or carbonate.
3. Granules, useful as a component in detergent formulations, each comprising at least 20% by weight of polycarboxylated polymer useful in such formulations and at least 20% by weight of zeolite and/or clay, the bulk density of said granules being at least 700 g/l, wherein the polycarboxylated polymer comprise homopolymers of dicarboxylic acids, anhydrides of cis dicarboxylic acids, and monocarboxylic acids; copolymers of the aforementioned carboxylic acids; and copolymers of one or more of the aforementioned carboxylic acids and unsaturated non carboxylic acids such as alkyl esters of acrylic or methacrylic acids, hydroxyalkyl esters of acrylic or methacrylic acids, acrylamide, methacrylamide, N-tertiary butyl acrylamide, N-methyl acrylamide, N, N-dimethyl acrylamide; acrylonitrile, methacrylonitrile, allyl alcohol, allyl sulfonic acid, allyl phosphonic acid, vinyl phosphonic acid, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, phosphoethyl methacrylate, N-vinyl pyrrolidone, N-vinyl formamide, N-vinylimidazole, ethylene glycol diacrylate, trimethylolpropane triacrylate, diallylphthalate, vinyl acetate, styrene, vinyl sulphonic acid and its salts, 2-acrylamido-2-methyl propane sulphonic acid and its salts, monomers of 1-olefins, and the polymer "POC".
4. Granules according to any preceding Claim, having a bulk density of at least 900 g/l.
5. Granules according to any preceding Claim, wherein the proportion of polycarboxylated polymer is from 20 to 40%, preferably 30%.
6. Granules according to any preceding Claim wherein the granule size is such that less than 50% by weight passes through 100 US mesh (mesh size 0.15 mm).
7. Granules according to any preceding Claim which absorb less than 20%, preferably less than 10%, of its weight in water when exposed to moisture, tested according to the method hereinbefore described.
8. The use of granules according to any preceding Claim as a component in a detergent formulation.
9. A detergent formulation containing polycarboxylated polymer in the form of granules according to any of claims 1 to 7.
10. A process for making polycarboxylated polymer-containing granules useful in a detergent formulation according to any of Claims 1-7 comprising mixing polycarboxylated polymer useful in detergent formulations with a liquid suitable for carrying or solubilizing said polycarboxylated polymer and at least one solid inorganic component itself useful in detergent formulations, wherein the ratio of polycarboxylated polymer to inorganic component is from 1:9 to 5:1, and subjecting the mixture to conditions of agitation and heat such that granules are formed; and wherein the mixture is introduced into a cylindrical chamber (2) containing a rapidly rotating axial shaft (16) carrying a series of blades (18), and heat applied to the mixture along at least a part of the length of said chamber.
11. Process according to claim 10, wherein the mixture is initially introduced into a first cylindrical chamber also containing a rapidly rotating axial shaft carrying a series of blades, in which chamber no heating takes place.
12. Process according to claim 10 or 11, wherein said heat is applied by one or both of hot air injected into said chamber (2) and heating of the internal surface of said chamber.

13. Process according to any one of claims 10 to 12 wherein said inorganic component is zeolite, clay or as defined in claim 2, and said polycarboxylated polymer is as defined in claim 3.
14. Process according to any one of claims 11 to 13 wherein said liquid is water.

#### Patentansprüche

1. Granalien, verwendbar als eine Komponente in Reinigungsmittelformulierungen, welche jeweils mindestens 10 Gew.-% eines in solchen Formulierungen verwendbaren polycarboxylierten Polymers und mindestens 20 Gew.-% mindestens einer in solchen Formulierungen ebenfalls verwendbaren wasserlöslichen anorganischen Komponente umfassen, wobei die Schüttdichte der Granalien mindestens 700 g/l beträgt.
2. Granalien nach Anspruch 1, wobei die anorganische Komponente eines oder mehrere von Sulfat, Carbonat, Phosphat, Silicat, Percarbonat oder Perborat, vorzugsweise Sulfat oder Carbonat ist.
3. Granalien, verwendbar als eine Komponente in Reinigungsmittelformulierungen, welche jeweils mindestens 20 Gew.-% eines in solchen Formulierungen verwendbaren polycarboxylierten Polymers und mindestens 20 Gew.-% Zeolith und/oder Ton umfassen, wobei die Schüttdichte der Granalien mindestens 700 g/l beträgt, wobei das polycarboxylierte Polymer Homopolymere von Dicarbonsäuren, Anhydriden von cis-Dicarbonsäuren und Monocarbonsäuren, Copolymere der vorgenannten Carbonsäuren und Copolymere von einer oder mehreren der vorgenannten Carbonsäuren und ungesättigten Nicht-Carbonsäuren wie Alkylester von Acryl- oder Methacrylsäuren, Hydroxyalkylester von Acryl- oder Methacrylsäuren, Acrylamid, Methacrylamid, N-tertiär-Butylacrylamid, N-Methylacrylamid, N,N-Dimethylacrylamid, Acrylnitril, Methacrylnitril, Allylalkohol, Allylsulfonsäure, Allylphosphonsäure, Vinylphosphonsäure, Dimethylaminoethylacrylat, Dimethylaminoethylmethacrylat, Phosphoethylmethacrylat, N-Vinylpyrrolidon, N-Vinylformamid, N-Vinylimidazol, Ethylenglykoldiacrylat, Trimethylolpropantriacyrylat, Diallylphthalat, Vinylacetat, Styrol, Vinylsulfonsäure und deren Salze, 2-Acrylamido-2-methylpropansulfonsäure und deren Salze, Monomere von 1-Olefinen und das Polymer "POC" umfasst.
4. Granalien nach einem vorhergehenden Anspruch, welche eine Schüttdichte von mindestens 900 g/l aufweisen.
5. Granalien nach einem vorhergehenden Anspruch, wobei der Anteil des polycarboxylierten Polymers 20 bis 40%, vorzugsweise 30%, beträgt.
6. Granalien nach einem vorhergehenden Anspruch, wobei die Körnchengröße derart ist, daß weniger als 50 Gew.-% durch US 100 mesh (Maschenweite 0,15 mm) passen.
7. Granalien nach einem vorhergehenden Anspruch, welche weniger als 20%, vorzugsweise weniger als 10%, ihres Gewichts in Wasser absorbieren, sofern sie Feuchtigkeit ausgesetzt werden, getestet gemäß dem zuvor beschriebenen Verfahren.
8. Verwendung der Granalien nach einem vorhergehenden Anspruch als eine Komponente in einer Reinigungsmittelformulierung.
9. Reinigungsmittelformulierung, enthaltend ein polycarboxyliertes Polymer in der Form von Granalien gemäß einem der Ansprüche 1 bis 7.
10. Verfahren zum Herstellen von in einer Reinigungsmittelformulierung verwendbaren, ein polycarboxyliertes Polymer enthaltenden Granalien gemäß einem der Ansprüche 1 bis 7, umfassend das Mischen von einem in Reinigungsmittelformulierungen verwendbarem polycarboxylierten Polymer mit einer Flüssigkeit, die zum Tragen oder Lösen des polycarboxylierten Polymers verwendbar ist, und mindestens einer festen anorganischen Komponente, die selbst in Reinigungsmittelformulierungen verwendbar ist, wobei das Verhältnis von polycarboxyliertem Polymer zur anorganischen Komponente 1:9 bis 5:1 beträgt, und das Unterwerfen des Gemisches unter Bedingungen von Umwälzung und Wärme derart, daß Granalien gebildet werden, und wobei das Gemisch in eine zylindrische Kammer (2) eingebracht wird, die einen schnellrotierenden axialen Schaft (16) enthält, der eine Serie von Blättern (18) trägt, und dem Gemisch Wärme entlang mindestens eines Teils der Länge der Kammer zugeführt wird.
11. Verfahren nach Anspruch 10, wobei das Gemisch anfänglich in eine erste zylindrische Kammer eingebracht wird, die ebenfalls einen schnellrotierenden axialen Schaft enthält, der eine Serie von Blättern trägt, wobei in der Kammer kein Erwärmen stattfindet.
12. Verfahren nach Anspruch 10 oder 11, wobei die Wärme mittels einem oder beiden von Einspeisen von Heißluft in die Kammer (12) und Erwärmen der inneren Oberfläche der Kammer zugeführt wird.
13. Verfahren nach einem der Ansprüche 10 bis 12, wo-



bei die anorganische Komponente Zeolith, Ton oder wie in Anspruch 2 definiert ist und das polycarboxylierte Polymer wie in Anspruch 3 definiert ist.

14. Verfahren nach einem der Ansprüche 11 bis 13, wobei die Flüssigkeit Wasser ist.

#### Revendications

1. Granulés utiles en tant que composant dans des formulations détergentes, comprenant chacun au moins 10 % en poids d'un polymère polycarboxylé utile dans ces formulations, et au moins 20 % en poids d'au moins un composant inorganique soluble dans l'eau, également utile dans ces formulations, la masse volumique apparente desdits granulés étant d'au moins 700 g/l.
2. Granulés selon la revendication 1, dans lesquels ledit composant inorganique est constitué d'un ou plusieurs des composants sulfate, carbonate, phosphate, silicate, percarbonate ou perborate, de préférence sulfate ou carbonate.
3. Granulés utiles en tant que composant dans des formulations détergentes, comprenant chacun au moins 20 % en poids d'un polymère polycarboxylé utile dans ces formulations et au moins 20 % en poids d'une zéolite et/ou d'une argile, la masse volumique apparente desdits granulés étant d'au moins 700 g/l, où le polymère polycarboxylé comprend des homopolymères d'acides dicarboxyliques, des anhydrides d'acides cis-dicarboxyliques, et des acides monocarboxyliques; des copolymères des acides carboxyliques mentionnés ci-dessus; et des copolymères d'un ou plusieurs des acides carboxyliques mentionnés ci-dessus et des acides insaturés non-carboxyliques, tels que des esters alkylés de l'acide acrylique ou de l'acide méthacrylique, des esters hydroxyalkyliques de l'acide acrylique ou de l'acide méthacrylique, l'acrylamide, le méthacrylamide, le N-tert-butylacrylamide, le N-méthylacrylamide, le N,N-diméthylacrylamide; l'acrylonitrile, le méthacrylonitrile, l'alcool allylique, l'acide allylsulfonique, l'acide allylphosphonique, l'acide vinylphosphonique, l'acrylate de diméthylaminoéthyle, le méthacrylate de diméthyl-aminoéthyle, le méthacrylate de phosphoéthyle, le N-vinylpyrrolidone, le N-vinylformamide, le N-vinylimidazole, le diacrylate d'éthylène-glycol, le triacrylate de triméthylolpropane, le phtalate de diallyle, l'acétate de vinyle, le styrène, l'acide vinylsulfonique et ses sels, l'acide 2-acrylamido-2-méthyl-propanesulfonique et ses sels, des monomères de 1-oléfines et le polymère "POC".
4. Granulés selon l'une quelconque des revendica-

tions précédentes, qui ont une masse volumique apparente d'au moins 900 g/l.

5. Granulés selon l'une quelconque des revendications précédentes, dans lesquels la proportion du polymère polycarboxylé est de 20 à 40 % et de préférence de 30 %.
6. Granulés selon l'une quelconque des revendications précédentes, dans lesquels la granulométrie est telle que moins de 50 % en poids passent par un tamis ayant une ouverture de maille de 0,15 mm (100 US mesh).
7. Granulés selon l'une quelconque des revendications précédentes, qui absorbent moins de 20 % et de préférence moins de 10 % de leur poids d'eau quand ils sont exposés à l'humidité, l'essai étant effectué par la méthode décrite ci-dessus.
8. Utilisation de granulés selon l'une quelconque des revendications précédentes, en tant que composant dans une formulation détergente.
9. Formulation détergente contenant un polymère polycarboxylé sous forme de granulés selon l'une quelconque des revendications 1 à 7.
10. Procédé de préparation de granulés contenant un polymère polycarboxylé, utiles dans une formulation détergente selon l'une quelconque des revendications 1 à 7, qui consiste à mélanger un polymère polycarboxylé utile dans des formulations détergentes avec un liquide capable de porter ou de solubiliser ledit polymère carboxylé, et au moins un composant inorganique solide, lui-même utile dans des compositions détergentes, où le rapport du polymère carboxylé au composant inorganique est de 1:9 à 5:1, et à soumettre le mélange à des conditions d'agitation et de chaleur telles qu'il y ait formation de granulés; et où le mélange est introduit dans une chambre cylindrique (2) contenant un arbre axial (16) en rotation rapide portant une série de pales (18), de la chaleur étant appliquée au mélange le long d'au moins une partie de la longueur de ladite chambre.
11. Procédé selon la revendication 10, dans lequel le mélange est initialement introduit dans une première chambre cylindrique contenant elle aussi un arbre axial en rotation rapide portant une série de pales, chambre dans laquelle aucun chauffage n'a lieu.
12. Procédé selon la revendication 10 ou 11, dans lequel ladite chaleur est appliquée par de l'air chaud injecté dans ladite chambre (2), ou par chauffage de la surface intérieure de ladite chambre, ou par

ces deux techniques.

13. Procédé selon l'une quelconque des revendications 10 à 12, dans lequel ledit composant inorganique est une zéolite, une argile ou un composant tel que défini dans la revendication 2, et ledit polymère polycarboxylé est tel que défini dans la revendication 3. 5
14. Procédé selon l'une quelconque des revendications 11 à 13, dans lequel ledit liquide est de l'eau. 10

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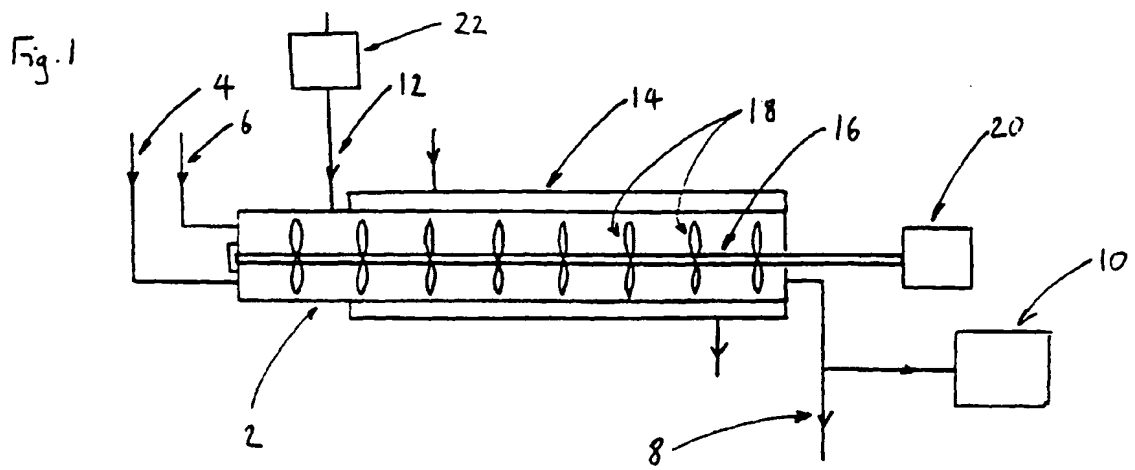
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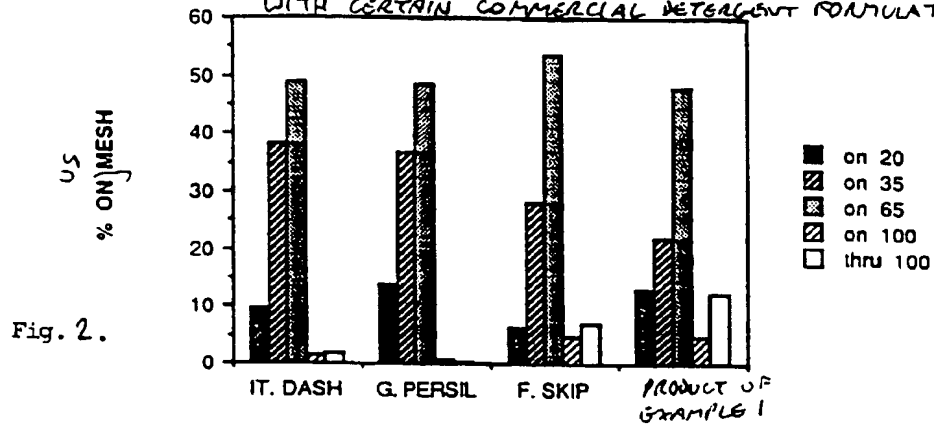
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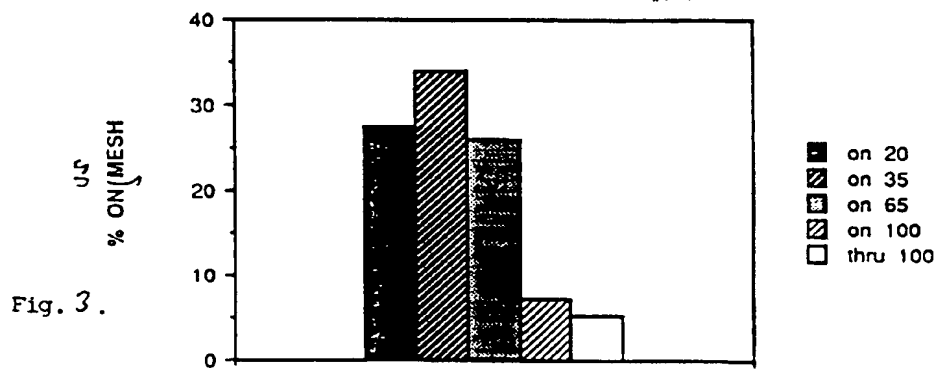
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GRANULOMETRY OF PRODUCT OF EXAMPLE 1 COMPARED  
WITH CERTAIN COMMERCIAL DETERGENT FORMULATIONS



GRANULOMETRY OF PRODUCT OF EXAMPLE 2



GRANULOMETRY OF PRODUCT OF EXAMPLE 3.

